



Kinetics of Natural Kaolinite as a Catalyst for Toluene Dry Reforming

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Abstract

This study aims to develop a kinetic model for natural kaolinite as a potential tar removal catalyst in biomass gasification processes. The catalyst was crushed, sieved (0.2mm), and analyzed using TGA, BET, and XRF. The apparent first-order kinetic parameters of the dry reforming reaction at temperatures ranging from 750 to 900°C under 1atm were used to determine kaolinite's catalytic activity. It was found that both dry reforming and thermal cracking reactions occurred simultaneously. Furthermore, the raw kaolinite catalyst significantly removed toluene (80% at 900°C), at activation energy and frequency factor of 209 kJ/mol and $5.86 \times 10^9 \text{ s}^{-1}$, respectively. Capitalizing on its catalytic activity in its natural form and its high efficacy as fluidized bed material, kaolinite can have great potential in primary and secondary tar reduction measures.

Paper type: Research paper

Keywords: Toluene, dry reforming, kaolinite, catalyst, tar, biomass, gasification.

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Introduction

The interest in exploiting biomass energy stems from a need to be independent of the supply of fossil fuels, which is characterized by volatile prices and high greenhouse gas emissions. After combustion technology, gasification is the most common for biomass energy exploitation (Briones-Hidrovo *et al.*, 2021). The latter converts biomass through partial combustion into a combustible gas known as producer gas or syngas, which can be used to produce heat, power, chemicals, and fuels. Besides the main components, H_2 , CO , CO_2 , H_2O , and CH_4 , the producer gas also contains gaseous impurities such as tar, particulates, and inorganic trace elements.

Tar removal, in particular, has been the subject of extensive research, leading to the development of tar reduction measures both within and downstream of the gasifier (Ashok *et al.*, 2020; Ren *et al.*, 2020; Abu El-Rub *et al.*, 2004; Devi *et al.*, 2003). This is because tar formation reduces syngas production and gas heating value. Furthermore, tar condensation at low temperatures can clog pipes, filters, catalyst beds, or engines (Horvat *et al.*, 2021; Li *et al.*, 2021). Tar, in general, refers to all organic substances heavier than benzene (Li *et al.*, 2021; Chan *et al.*, 2019). Its levels are required to be less than 100 mg/Nm³ for gas engines, less than 50 mg/Nm³ for gas turbines, and less than 1 ppmv for the Fischer-Tropsch fuel synthesis process (Haro *et al.*, 2013). Typical tar produced from biomass gasification includes several main components, the most important of which are toluene (14%), and naphthalene (10%) whose proportions are affected by the type of biomass and the gasification conditions (Ashok *et al.*, 2020). Therefore, the behavior of tar interactions can be studied through the behavior of these components during reformulation using catalysts. Among the various types of tar, toluene is the most prevalent compound formed as a result of catalytic reformation (Gao *et al.*, 2021; Du *et al.*, 2018).

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Gas cleaning with high-temperature catalytic conditioning enhances the efficiency of industrial applications of biomass gasification for the production of energy and chemicals (Ashok *et al.*, 2020). This entails using a narrow temperature range for both gas treatment and biomass conversion to preserve the thermal energy content of the producer gas. Because of the high activation energies (250–350 kJ/mol), the uncatalyzed tar reforming and cracking reactions require temperatures above 1200°C (Basu, 2010). Catalysts enable steam and dry reforming reactions to remove tar from producer gas at relatively low temperatures. Equations 1–3 show the toluene reforming and thermal cracking reactions. Furthermore, carbon dioxide impedes the advancement of gasification technology because it lowers the heating value of the produced gas. (Chen *et al.*, 2021). As a result, tar removal via dry reforming converts both tar and carbon dioxide, improving both the quality of the producer gas and the efficiency of the gasification technology.



The catalytic performance in tar reforming has been investigated for a variety of materials, including nickel-based catalysts, iron-based catalysts, new metal catalysts, dolomite, olivine, and char (Ashok *et al.*, 2020; Abu El-Rub *et al.*, 2004). Aluminosilicates, such as kaolinite are conveniently accessible, inexpensive, have a large specific surface area and a high cation exchange capacity (Abukhadra *et al.*, 2018), and can be used in catalytic gasification processes (Abu El-Rub *et al.*, 2004). Moreover, adding additives such as iron oxide, magnesium carbonate, and calcium carbonate to the raw pure clay catalyst can improve the catalytic activity of kaolinite to the point where the tar in the gasification system is completely removed (Šuhaj *et al.*, 2019).

Kaolinite mineral is abundantly available in several Jordanian locations, including Esh-Shidiya, Ruseifa, El-Hasa, and Wadi Samou (Khouri *et al.*, 1988). This mineral possesses the physical and chemical properties that make it a viable catalyst for tar removal in biomass gasification systems. The purpose of this paper (**Figure 1**) was to investigate natural Jordanian kaolinite as a potential catalyst for removing tar produced in biomass gasification processes. To accomplish this, kaolinite was first characterized using physical and chemical analyses such as TGA, BET, and XRF. The catalytic activity of kaolinite for tar removal was then determined by evaluating the apparent first-order kinetic parameters for dry reforming of toluene model tar component at temperatures ranging from 750 to 900°C under atmospheric pressure of carbon dioxide and nitrogen gas.

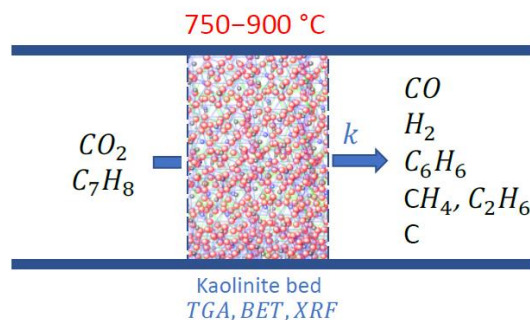


Fig. 1 Illustration of the research objectives of characterization of natural kaolinite and finding the kinetics of dry toluene reforming in a fixed bed of natural kaolinite

1 Materials and Methods

1.1 Kaolinite characterization

Kaolinite Samples were collected from the El-Hasa deposit, located 140km south of the capital Amman. These samples were air-dried and ground to an average particle size of 0.2mm. Thermogravimetric analysis (TGA) was performed using a TG 209 F1 Libra® Thermogravimetric analyzer system (Netzsch, Germany) from room temperature to 900°C under an ambient atmosphere of nitrogen at heating rates of 10, 50, and 100°C/min. Nitrogen adsorption was used to measure the specific surface area of samples applying the Brunauer–Emmett–Teller (BET) method using the Autosorb-1-C model (Quantachrome Instruments, USA). X-ray fluorescence was used to analyze the chemical composition of the major metal oxides present in kaolinite using a sequential wavelength dispersive XRF spectrometer (Bruker S4 Pioneer, Germany).

1.2 Reactor setup

The reactor used in this experiment is a plug flow reactor with negligible pressure drop or expansion. The experimental reactor setup is shown in **Figure 2**, which consists of three basic sections: A) feed gas mixing lines carrying nitrogen and carbon dioxide, as well as a toluene saturation glass unit, B) a carbon steel fixed-bed reactor (ID=3.8cm, OD=4.2cm, H=85cm) surrounded by a compact

vertical tube furnace model EVC 12/450 (Carbolite, UK), and C) a gas chromatography (GC) instrument, model GC-2014 (Shimadzu, Japan) with two detectors: thermal conductivity (TCD) and flame ionization (FID).

The experiment was repeated twice at each reactor temperature, and the results were averaged. The setup is operated according to the parameters shown in **Table 1**. The flow of gases from cylinders is controlled by pressure regulators followed by gas flowmeters. One of the nitrogen streams is passed through the toluene saturation unit, whose temperature is set at 40°C and controlled electrically by heating the water bath surrounding the unit. Gas lines are assembled into one line linked to the top of the reactor as the reactor feed. The required weight of kaolinite is prepared and placed inside the reactor on top of quartz fritted disc (35mm diameter) fitted in the middle of the reactor. The reactor is then tightly connected to the steel lines that carry the input and output. The temperature is then raised to the required level by adjusting the final temperature and heating rate. The lines that connect to the inlet and outlet of the reactor are also heated using heating tapes that can be regulated to a temperature of up to 250°C in order to prevent toluene condensation. Feed gas can be introduced either through the reactor or through the reactor bypass. Whereas the output gas from the reactor or through the bypass line is vented or analyzed using the GC where organic gases are analyzed using FID and inorganic gases using TCD.

1.3 Kinetic model

The most effective catalytic tar conversion reactions are the steam and dry reforming reactions according to Equations 2 and 3. However, the focus of this work is on the dry reforming reaction since it has a significant impact on syngas quality. As a result, an excess of CO₂ (80 vol.%) was fed into the reactor, causing toluene to become the limiting reactant and the reaction to be assumed a pseudo-first-order reaction. The estimation of the kinetic parameters was explained elsewhere (Abu El-Rub *et al.*, 2008; Abu El-Rub *et al.*, 2015; Abu El-Rub *et al.*, 2019). However, the model can be summarized by Equations 4–9:

$$-\frac{dC_{C_7H_8}}{dt} = k \cdot C_{CO_2} \cdot C_{C_7H_8} \quad (4)$$

$$-\frac{dC_{C_7H_8}}{dt} = k_{app} \cdot C_{C_7H_8} \quad (5)$$

$$X = \frac{C_{in} - C_{out}}{C_{in}} \quad (6)$$

$$k_{app} = \frac{-\ln(1-X)}{\tau} \quad (7)$$

$$k_{app} = A \cdot e^{-E_a/R \cdot T} \quad (8)$$

$$\ln(k_{app}) = \ln(A) - \frac{E_a}{R} \cdot \frac{1}{T} \quad (9)$$

Where, $C_{C_7H_8}$, C_{CO_2} are the concentrations of toluene and carbon dioxide in the output gas respectively.

X is the toluene conversion based on the input (C_{in}) and output (C_{out}) toluene concentrations to and out of the reactor.

τ is the gas residence time in the catalyst bed, s.

k_{app} is the apparent pseudo-first-order kinetic constant, s⁻¹.

A is the frequency factor, s⁻¹.

E_a is the activation energy, J/mol.

R is the gas constant, J/mol K.

T is the catalyst bed temperature, K.

Table 1 Experimental operating conditions.

Parameter	Symbol	Value	Unit
Reactor temperature	T	750-900	°C
Reactor pressure	P	1	atm
Gas residence time in the catalyst bed	τ	s	0.3
Feed gas composition (CO ₂ , N ₂)*	y	80%, 20%	vol. %
Feed toluene concentration	C _{in}	10	g/Nm ³

*Excluding toluene content

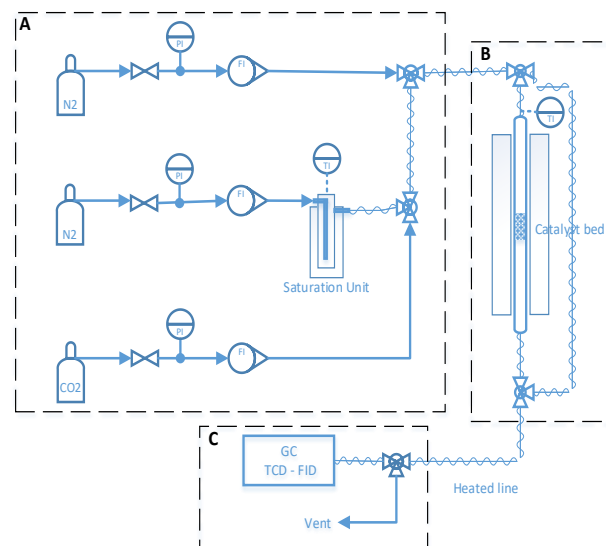


Fig. 2 Scheme of toluene dry reforming setup: A) feed section, B) reactor section, C) gas analysis section.

2 Results and Discussion

2.1 TGA

The thermal stability of the kaolinite catalyst was tested in the hot gas cleaning temperature range of 750-900°C. The weight loss and surface area of the calcined material are affected interdependently by the final calcination temperature and heating rate. Thermogravimetric analysis (TGA) was performed at temperatures ranging from room temperature to 900°C under 1 atm of nitrogen at heating rates of 10, 50, and 100°C/min. **Figure 3** presents the weight loss profile of kaolinite at the previously mentioned heating rates. The weight loss of kaolinite samples can be attributed to dehydration, which is followed by mineral carbonate decomposition (Shun *et al.*, 2021). The adsorbed and bound water were removed at temperatures up to 450°C. However, above 450°C, demineralization occurred due to the breakdown of elemental bonds. Furthermore, the weight loss at 900°C was in the range of 11.3-11.9wt.% for heating rates of 50°C/min and 100°C/min, respectively. The lower loss at the highest heating rate can be attributed to the short residence time available for vapors to escape from the particles' pores. However, there is no consistent trend in the two lower heating rates. The kaolinite material was found to be nonsticky after calcination tests, which is considered an advantage. (Öhman *et al.*, 2000; Vuthaluru *et al.*, 1999) reported the formation of less viscous ash and found that kaolinite is more effective than many fluidized-bed materials in mitigating bed agglomeration, including dolomite, silica sand, and bauxite.

2.2 BET

Because the TGA analysis influenced kaolinite weight loss, the specific surface area is most likely influenced as well. **Figure 4** shows the effect of heating rate on the specific surface area of calcined kaolinite at a final temperature of 900°C and a heating rate of 10-100°C/min. The resultant BET surface area is inversely proportional to the heating rate, with a maximum specific area of 18m²/g at 10°C/min and a minimum specific area of 1.4m²/g at 100°C/min. This is due to the extreme removal of gases and vapors at high heating rates, which can destroy pores and thus reduce specific surface area. Accordingly, a low heating rate (10°C/min) was used in the catalytic dry reforming experiments of toluene. These findings are comparable to the 15.35m²/g BET determined by (Ji *et al.*, 2021) for the raw kaolinite (source: Ward's Science, USA) and 13.63m²/g determined by (Rosadi *et al.*, 2020) for the pretreated and calcined kaolinite (source: Ranong, Thailand) at 500°C. Running the dry reforming reaction at a low heating rate is a beneficial process since it provides the residence time required for reaction completion (Basu, 2010).

2.3 XRF

Kaolinite is a clay mineral that is composed of 1:1 layered dioctahedral aluminum silicate and belongs to the kaolin minerals group (Guggenheim *et al.*, 2006). The ideal formula of kaolinite is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ and it is associated in nature with other metals such as zeolite and quartz (Lázaro, 2015). Furthermore, the composition of kaolinite varies depending on its geological origins and the region in which it is found. Elements like K, Ti, Fe, Mg, Ca, and Mn as well as impure phases like quartz are common in natural kaolinite and affect its chemical properties (Zhu *et al.*, 2019). **Table 2** shows the XRF analysis of major metal oxides in the tested Jordanian kaolinite. The main metal oxides are silica and alumina with a ratio of 2.2. Other metal oxides, such as those of alkali metals and iron, exist in small percentages but can play an important role in promoting catalytic activity (Abu El-Rub, *et al.*, 2004).

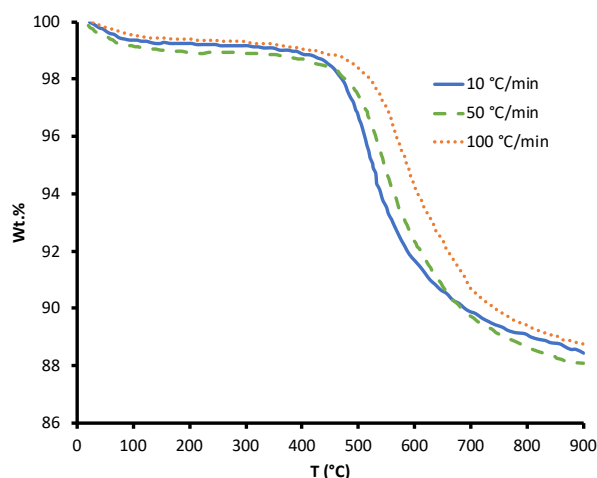


Fig. 3 Thermogravimetric analysis (under nitrogen) of kaolinite decomposition curves at heating rates of 10, 50, and 100 °C/min.

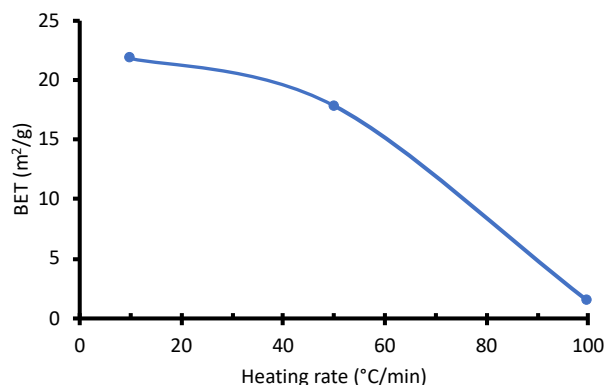


Fig. 4 Effect of heating rate on kaolinite surface area (BET).

Table 2 XRF analysis of major metal oxides and loss on ignition (LOI) of Jordanian kaolinite (wt.%).

Metal Oxide	SiO ₂	Al ₂ O ₃	K ₂ O	TiO ₂	Fe ₂ O ₃	MgO	CaO	P ₂ O ₅	Na ₂ O	MnO	L.O.I
Wt. %	57.4	26.1	1.47	1.13	1.05	0.223	0.141	0.121	0.01	0.001	11.6

2.4 Kinetics of dry reforming

Toluene is a stable component of tar produced at high gasification temperatures. Furthermore, as demonstrated by (Ashok *et al.*, 2020) its catalytic conversion is a complex process. The major products of the catalytic dry reforming of toluene at 900°C employing natural kaolinite as a catalyst are shown in **Figure 5**. The results confirm the occurrence of both the dry reforming reaction (Equation 2) and to some extent thermal cracking (Equation 3). The dry reforming reaction was demonstrated by the presence of CO and H₂ (**Figure 5-A**). In contrast, the thermal cracking was verified by the presence of some black carbon (coke) deposited on the catalyst particles, as well as the detected gases of methane-ethane, benzene, and traces of m-xylene (**Figure 5-B**). The only quantified component was toluene as the aim is to study the toluene conversion and to find out its kinetic equation exemplified in Equation 4. The other gases were not quantified because the measurement accuracy of gases such as ethane and methane were not high enough to be reported. However, it was found that the relative amounts of gases increased with increasing the bed temperature, which can be related to the higher rate of reactions (reforming and cracking) at higher bed temperatures. Nevertheless, it would be advantageous in a future work to conduct a study tracking the evolved gases out of these reactions, which will help also in getting a better understanding the mechanism of these reactions. In addition, the thermal cracking reactions are anticipated to be minimal at temperatures below 1200°C, according to (Basu, 2010). The observed kinetics was therefore presumed to be for the toluene dry reforming reaction.

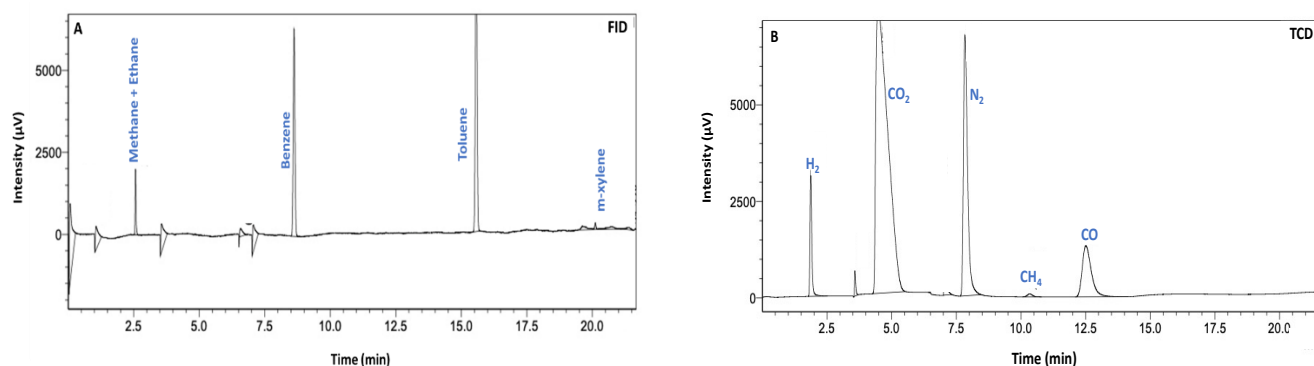


Fig. 5 GC gas analysis of the output gases resulted from the dry reforming reaction of toluene in the presence of the kaolinite catalyst bed at 900°C. (A) FID analysis for organic content. (B) TCD analysis for inorganic content.

The catalytic toluene conversion was carried out in the hot gas cleaning temperature range that is close to that of gasification (750–900°C). The percentage conversion of toluene under the prescribed conditions is shown in **Table 3**. The conversion of toluene was weak (7%) at 750°C due to the strong C–C bond in the toluene cyclic structure. However, the conversion increased significantly above this temperature because the catalytic activity of kaolinite was greatly enhanced reaching 80% at 900°C. Kaolinite accelerates the conversion of toluene by lowering the activation energy of the dry reforming reaction of toluene. A pseudo-first-order kinetic model was assumed since the catalytic dry reforming reaction is heterogenous. Equation 6 uses the conversion values from **Table 3** to estimate the values of the apparent kinetic constant. Equation 9 was plotted to find the apparent kinetic parameters, as illustrated in **Figure 6**. In addition, error bars based on the standard deviation of the averaged points are displayed. The activation energy and the frequency factor were found to be 209 kJ/mol and $5.86 \times 10^9 \text{ s}^{-1}$, respectively.

Table 3 Toluene conversion averages at various catalyst bed temperatures.

Temperature (°C)	Average Conversion (%)
750	7.0
800	27
850	73
900	80

For kaolinite-catalyzed dry reforming of toluene, no kinetic data to compare with could be found in the literature. Although toluene was significantly removed by natural kaolinite, it was not entirely removed. However, kaolinite might be regarded as an efficient material in primary tar reduction methods if we combine its catalytic activity with its high efficacy as a fluidized bed material (in-situ). Moreover, modifying natural kaolinite by impregnation with different percentages of ions and metals can greatly improve its catalytic activity and facilitates its use in secondary tar reduction measures (downstream of the gasifier). Furthermore, the most significant benefit of kaolinite catalyst is that it is a natural substance that is readily available in Jordan and other parts of the world. When used in the removal of tar, this creates a catalyst that has essentially no environmental impact. Chemical catalysts, regardless of their performance, usually necessitate the use of chemicals and energy during their creation. As a result, any synthesized chemical catalyst's life cycle analysis has a negative influence on the environment in terms of greenhouse gas emissions. The chemical process for catalyst fabrication is rather complicated (Eijsbouts *et al.*, 2008). It includes chemical purchase, feedstock storage, production, storage, waste management, transportation, etc. All these steps are energy intensive and generate waste chemical substances that plague the environment. Therefore, kaolinite could be considered a green catalyst that provides efficient and effective tar removal with zero to minimal impact on the environment once it is implemented.

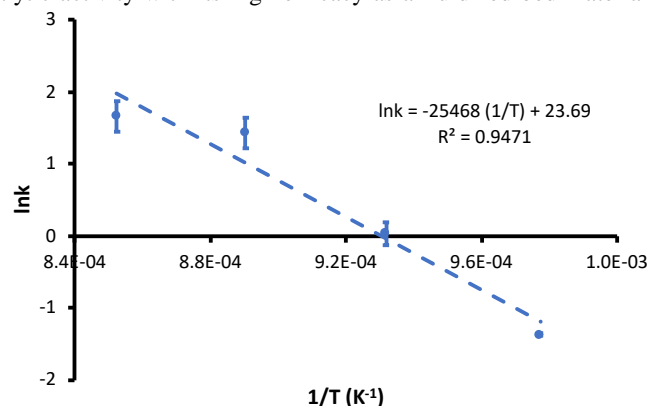


Fig. 6 Pseudo-first-order apparent kinetic parameters for toluene dry reforming reaction using Jordanian kaolinite as a catalyst.

Conclusions

In the present study, the catalytic activity of natural kaolinite was characterized by finding the apparent first-order kinetic parameters of the dry reforming reaction of toluene as a tar model component in the temperature range of 750–900°C under atmospheric pressure of carbon dioxide and nitrogen. It was concluded that the catalytic conversion of toluene is a complex reaction. However, it was evident that both dry reforming and minimal thermal cracking reactions occurred simultaneously. The activation energy and frequency factor for the pseudo-first-order kinetic constant for toluene dry reforming reaction catalyzed by kaolinite was found to be 209kJ/mol and $5.86 \times 10^9 \text{ s}^{-1}$, respectively. Moreover, the BET-specific surface area of the calcined kaolinite was inversely proportional to the heating rate, with a maximum of 18m²/g at 10°C/min. Even though only 80% of the toluene was removed by raw kaolinite activity (at 900°C), the amount still represents a considerable percentage. Considering both catalytic activity and high efficacy as fluidized bed material, kaolinite can have a great potential in primary tar reduction measures (inside the gasifier). On the other hand, it is expected by modifying the natural kaolinite through impregnation with different proportions of metal oxides, the catalytic activity can be greatly improved, which facilitates its use in secondary tar reduction measures (downstream of the gasifier).

Nomenclature

A	=Frequency factor	[s ⁻¹]
BET	=Brunauer–Emmett–Teller	[-]
C _{C7H8}	=Toluene concentration	[g/Nm ³]
C _{CO2}	=Carbon dioxide concentration	[g/Nm ³]
C _{in}	=Feed toluene concentration	[g/Nm ³]
C _{out}	=Output toluene concentration	[g/Nm ³]
E _a	=Activation energy	[J/mol]
FID	=Flame ionization detector	[-]
GC	=Gas chromatography	[-]
H	=Reactor height	[cm]
ID	=Internal diameter	[cm]
k _{app}	=Apparent pseudo-first-order kinetic constant	[s ⁻¹]
OD	=Internal diameter	[cm]
P	=Reactor pressure	[atm]
R	=Gas constant	[J/mol K]
T	=Catalyst bed temperature	[K]
TCD	=Thermal conductivity detector	[-]
TGA	=Thermogravimetric analysis	[-]
X	=Toluene conversion	[%]

XRF	=X-ray fluorescence	[-]
τ	=Gas residence time in the catalyst bed,	[s]
y	=Feed gas composition (CO ₂ , N ₂)	[vol.%]

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